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Use of Crystalline Boron as a Burn Rate Retardant toward the Development of Green-Colored Handheld Signal Formulations

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Use of Crystalline Boron as a Burn Rate Retardant toward the Development of Green-Colored Handheld Signal Formulations

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Keywords: burn rate retardant, crystalline boron, handheld signals, pyrotechnics

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Introduction

Handheld signals (HHS) are used in signaling troop movements and aircraft. They are meant to attract attention, day or night, and serve as a beacon for rescuers to identify the positions of military personnel. HHS technologies find use in both training exercises and combat situations, and improvements are being sought to advance existing HHS technology. Barium nitrate is widely used in pyrotechnic applications, including illuminating candles and civilian fireworks. In addition to its significant oxidizing capability, barium nitrate is used to cause the emission of green light in pyrotechnics. When barium reacts with chlorine in the excited state, metastable barium chloride (BaCl) is produced, serving as the green light emitter in pyrotechnic formulations [1]. Although they are superior green light emitters in pyrotechnics, many barium-based compounds are hazardous to human health [2]. Barium has been found to cause muscle cramps, cardiovascular problems, and respiratory complications [3,4]. The problem of environmental pollution by pyrotechnics has been extensively studied by Klapötke and his student Steinhäuser [5,6]. It has been observed that most of the barium compounds produced during combustion (BaO , Ba(OH)_2 , BaCl_2) are water soluble and are readily absorbed by the body. Furthermore, an unexpected problem of barium-containing pyrotechnics could be the accumulation of radium, which arises from contaminated barium ores used in the manufacturing of barium nitrate [7]. For these reasons, the removal of barium from pyrotechnic formulations is desirable.

To mitigate the toxicity issues of the barium-containing HHS formulations, a program was initiated by Armament Research, Development and Engineering Center (ARDEC) to develop barium-free green light-emitting pyrotechnic formulations. These formulations would, in principal, derive their energy and color from potassium nitrate oxidizer and amorphous boron as the fuel. It is believed that amorphous boron, when reacted with oxygen, forms metastable boron oxide (BO_2) in the excited state, which is responsible for pyrotechnic green light emission. Although amorphous boron is a known green light emitter in

pyrotechnics [8], it is a highly reactive fuel when subjected to a thermal stimulus in the presence of oxygen. Due to its high reactivity, the ability to control the burn time of amorphous boron-based pyrotechnics can be challenging.

To retard burn rates of many pyrotechnic munitions, altering the particle sizes of oxidizers and fuels, altering the oxidizer–fuel ratio, and increasing the percentage of binder used are among the most common approaches used [9]. Although the use of additives to chemically influence the pyrotechnics has successfully retarded burn rates in several formulations [10], the use of crystalline boron additive and its effect on burn rates in pyrotechnics has never been explored.

Experimental

Materials

Mg 30/50, $\text{Ba}(\text{NO}_3)_2$ was purchased from Reade (Manchester, NJ). PVC and KNO_3 , were purchased from Hummel Croton (South Plainfield, NJ). Crystalline boron and amorphous boron were purchased from Alfa Aesar (Ward Hill, MA). Laminac 4116 was purchased from Ashland Chemical Company (Covington, KY). Lupersol was purchased from Norac (Azusa, CA). Epon 828 and Epikure 3140 were purchased from Hexion Specialty Chemicals (Columbus, OH).

Preparation of M125A1 Formulations

Twenty-gram formulations were prepared by weighing out the chemicals according to their respective weight percentages in the HHS formulations. After drying the chemicals overnight, they were introduced to a binder system (95% Laminac 4116/5% Lupersol or 80% Epon 828/20% Epikure 3140), and the mixture was hand-blended for 20 min. After hand-mixing, Laminac 4116/Lupersol-based formulations were dried in the oven overnight at 60°C, and Epon828/Epikure 3140-based formulations were dried in air for 2–3 h at ambient temperature before pressing.

Formulations were weighed out in two 2-g increments and were pressed into pellets with a diameter of 1.27 cm and a

height of 2.50 cm with a tooling die and manual press at a consolidation dead load of 893 kg. Between 3.99 and 4.02 g of energetic material was used per pellet, and five pellets were tested per formulation.

Characterization

Optical emissive properties of these formulations were characterized using both a single-element photopic light detector and a 2,048-element optical spectrometer. The light detector used was manufactured by International Light (Peabody, MA) and is composed of an SED 033 silicon detector (33 mm² area silicon detector with quartz window) coupled to a photopic filter (Y-filter) and a field of view-limited hood (H-hood). The current output of the detector was converted to voltage using a DL Instruments (Ithaca, NY) 1211 transimpedance amplifier. Voltage output was collected and analyzed from the amplifier using an NI-6115 National Instruments (Austin, TX) datacard and in-house-developed LabviewTM-based data acquisition and analysis software.

Results and Discussion

An investigation was launched to modify the U.S. Army's in-service M125A1 HHS formulation (Table 1) so that the new formulations would be barium free yet exhibit promising pyrotechnic activity. In the baseline formulation, barium nitrate served as both an oxidizer and a colorant. Magnesium provided the main fuel source in the formulation. It was a grey

Table 1
M125A1 baseline formulation

Components	Weight, %
Barium Nitrate	46
Magnesium 30/50	33
Polyvinyl Chloride	16
Laminac 4116/Lupersol	5

body emitter and formed magnesium oxide (MgO) in a highly exothermic process upon reacting with barium nitrate. Although it served as a low-energy fuel, polyvinyl chloride (PVC) is a known color enhancer and participated as a chlorine donor during the combustion process. Another reason for the utilization of PVC was the volatilization of incandescent MgO by transforming it to the more volatile MgCl species [5]. When chlorine and barium reacted during the combustion process, BaCl formed, and this species provided green light-emitting pyrotechnic qualities. Laminac 4116/Lupersol was the binder system, and its role was to ensure homogeneity among oxidizers and fuels. Use of a binder system was also necessary to mitigate sensitivity issues and safety hazards that typically arise when oxidizers and fuels are consolidated.

Because the removal of barium nitrate was a high priority in developing an environmentally benign M125A1 formulation, an immediate problem arose because barium nitrate provides oxidizing and colorant qualities to the formulation. To produce a suitable green light-emitting pyrotechnic, it was decided to replace the barium nitrate/magnesium 30/50 oxidizer/fuel system with an oxidizer/fuel system consisting of potassium nitrate/amorphous boron (Table 2). PVC would no longer be needed in the new formulation because the liberation of chlorine would not serve an added benefit toward enhancing green light emission. The Laminac 4116/Lupersol binder system was also replaced due to its own environmental, human health, and availability concerns [11]. The Laminac 4116/Lupersol binder system contains styrene monomer, is a known carcinogen, has

Table 2
Barium-free M125A1 formulation A

Components	Weight, %
Potassium Nitrate	83
Amorphous Boron	10
Epon 828/Epikure 3140	7

a limited shelf life, and has been identified as a single-point failure (spf). An epoxy-based binder system, Epon 828/Epikure 3140, was chosen as the replacement (Table 2).

To establish a relevant data point, formulation A was tested and evaluated against the performance of the barium-containing baseline M125A1 green star cluster formulation. The performances of these two formulations are summarized in Table 3. The burn time of formulation A was significantly shorter compared to the burn time of the baseline formulation. As expected, the faster burning formulation A had a higher average luminous intensity compared to the baseline. The dominant wavelength values of these formulations were also comparable from the standpoint of green light emission. Although formulation A had a lower spectral purity compared to the baseline, it is highly unlikely that such a change in spectral purity would be detected by the naked eye.

Because formulation A burned so quickly, it became necessary to retard the burn rate by addition of a burn rate modifier or additive. Crystalline boron is a known allotrope of amorphous boron. Whereas amorphous boron reacts in the presence of dilute nitric acid at ambient temperature, crystalline boron undergoes no reaction under similar conditions [12]. Although crystalline boron slowly reacts in the presence of concentrated nitric acid under boiling conditions, it fails to react when treated with boiling hydrofluoric and hydrochloric acids [13].

Table 3
Performance of formulation A and the M125A1
baseline formulation

Formulation	Average burn time (sec)	Average luminous intensity (cd)	Average dominant wavelength (nm)	Average spectral purity (%)
Baseline	8.78	816.90	554.30	66.40
A	2.39	1706.50	567.30	55.00

The chemically inert nature of crystalline boron made its use as an additive to prolong burn times an attractive option.

To survey how crystalline boron would affect burn time, several formulations (B–I) were prepared. In these formulations, the weight percentages of potassium nitrate and Epon 828/Epikure 3140 binder system were kept constant, and the total boron content of the formulations—consisting of both amorphous boron and crystalline boron—was kept at 10% (Table 4).

The results of using crystalline boron to prolong the burn time of the barium-free formulations are summarized in Table 5. Burn time increases were observed as the amount of crystalline boron in a formulation increased. Presumably, the inclusion of crystalline boron in a formulation reduced the overall energy of the pyrotechnic. This direct relationship demonstrated the tunability that was possible by using crystalline boron in pyrotechnic munitions to control burn time. It is worth noting that a formulation was prepared according to Table 4 in which crystalline boron served as the only boron source (10% crystalline boron/0% amorphous boron). This formulation failed to fire, further confirming the inability of crystalline boron to contribute substantial energy to a pyrotechnic system.

The addition of crystalline boron (and the reduction of amorphous boron) had a negligible effect on the average dominant wavelength and average spectral purity values. Predictably, the longer burning pyrotechnic munitions were associated with a decrease in average luminous intensity values. Formulation F exhibited the closest average burn time and luminous intensity values when compared to the baseline formulation.

Table 4
General composition makeup of formulations B–I

Components	Weight, %
Potassium Nitrate	83
Amorphous/Crystalline Boron	10
Epon 828/Epikure 3140	7

Table 5

Performance of the baseline formulation and formulations A–I

Formulation	Average burn time (sec)	Average luminous intensity (cd)	Average dominant wavelength (nm)	Average spectral purity (%)
Baseline	8.78	816.90	562.30	66.40
A	2.39	1706.50	567.30	55.00
B	3.21	1580.60	564.60	54.70
C	4.01	1124.10	563.70	53.60
D	4.95	1608.00	562.90	52.80
E	6.27	1338.90	563.00	55.70
F	7.90	806.70	563.20	56.60
G	9.55	574.70	563.10	58.40
H	10.12	272.90	564.60	54.70
I	13.92	161.20	564.50	56.10

Formulation F was identified as the best candidate to test in a full-up prototype capacity in the hopes of meeting or exceeding the military specification requirements for green HHS.

Conclusions

A number of barium-free formulations have been developed to replace in-service green star HHS formulations. The use of crystalline boron to prolong burn times was significant because it demonstrated its potential in achieving tunable pyrotechnic munitions. Because its chemically inert nature was demonstrated in high-temperature pyrotechnic formulations, crystalline boron has the potential use in other pyrotechnic munitions in which prolonging burn rate is a pressing concern.

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